

TAILORING INTEGRATED LAYERED AND SPINEL ELECTRODE STRUCTURES FOR HIGH CAPACITY LITHIUM-ION CELLS

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Project ID # BAT049

Overview

Timeline

- Start date: FY16
- End date: FY18
- Percent complete: 100%

Budget

- Total project funding: 100% DOE
- FY18 Funding:
 - Composite Electrodes: \$400K
 - Spinel Components: \$400K

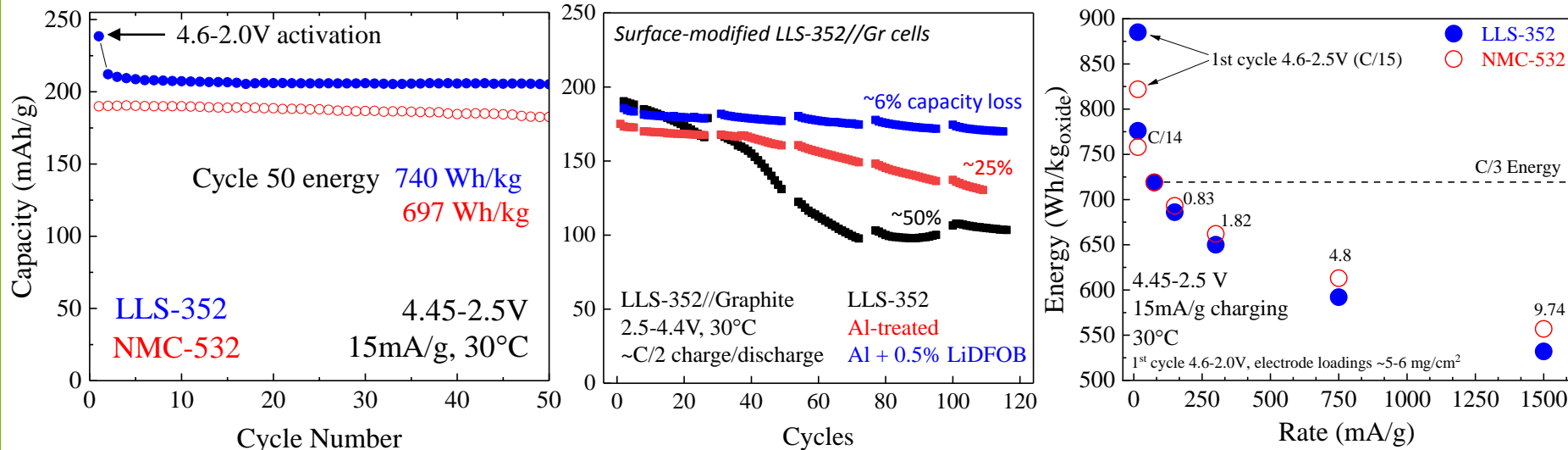
Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

■ Partners

- CSE, Argonne: Michael M. Thackeray, Eungje Lee, Arturo Gutierrez, Bob Jin Kwon, Fulya Dogan-Key, Roy Benedek, John Zhang
- ES, Argonne: Devika Choudhury, Anil Mane, Jeff Elam
- UIC: Soroosh Sharifi-Asl, Reza Shahbazian-Yassar
- ANL industrial partners

Energy, stability, and rate performance of Mn-rich cathodes



- Work from this project (above) has demonstrated that Mn-rich electrodes can achieve parity with NMCs such as NMC-532 in terms of energy, stability, and rate
- Cost and safety are still the main drivers in the development of electric vehicle batteries, *Mn-rich electrodes offer advantages in both areas*
- Supply and demand are a growing concern with respect to the future of Ni-rich cathodes

Safety, Cost, Energy, Supply and Demand could be critical issues for Ni/Co chemistries
 – *Mn-rich alternatives may provide competitive, necessary, future options*

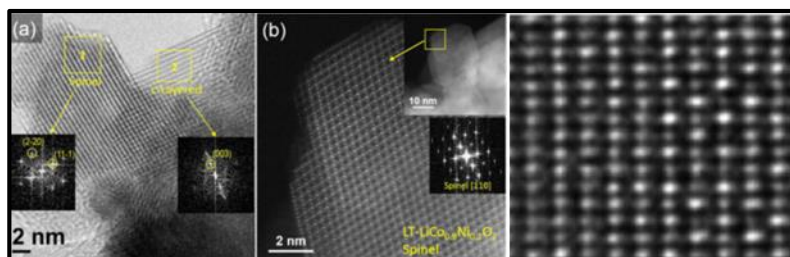
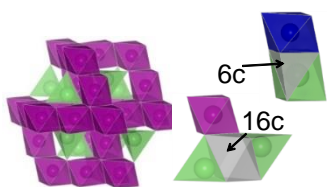
Milestones

- Explore the energy content, and stabilization thereof, of moderate Li_2MnO_3 -content ($25\% < x < 50\%$) $y[x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2] \bullet (1-y)\text{LiM}_2\text{O}_4$ ($\text{M}=\text{Mn, Ni, Co}$), layered-layered and layered-layered-spinel electrodes; target capacity ≥ 220 mAh/g. **Complete/ongoing.**
- Study reactions conditions of Mn-rich precursors in order to realize dense particles with optimal composition, size, morphology, and porosity. **Ongoing**
- Identify surface-treatment strategies that enable layered-layered-spinel electrodes to maintain high capacities (≥ 220 mAh/g) and high rate performance (~ 200 mAh/g at 1C). **Achieved/ongoing.**
- Demonstrate oxide energy densities ≥ 750 Wh/kg_{oxide} in full-cell testing of surface-modified, layered-layered-spinel electrodes. **Achieved/ongoing.**
- Explore and identify promising spinel-based structures as integrated components in the design of new layered-layered-spinel cathodes. **Achieved/ongoing.**

Correlated milestones aimed at achieving and demonstrating attractive, practical performance of Mn-rich electrodes

Approach

- Exploit the concept and optimize the performance of **structurally-integrated** “composite” electrode structures with a prime focus on “layered-layered-spinel” (LLS) materials.



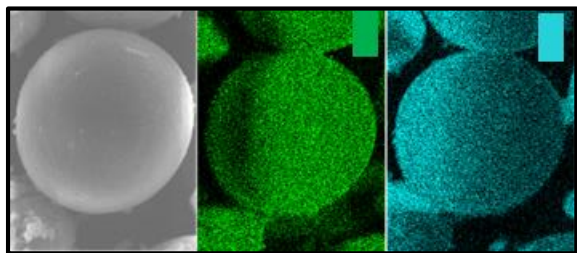
Compatibility of cubic-close-packed planes

Complex, integrated, layered-layered-spinel structures

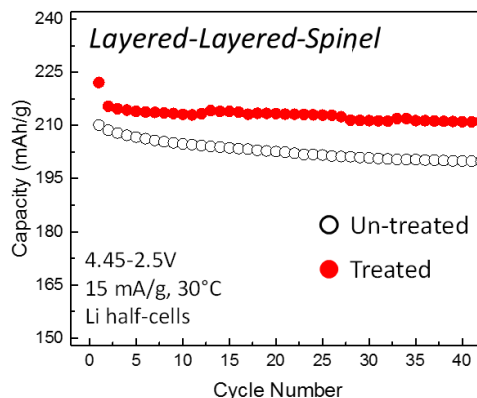
Enable:

1. High first-cycle efficiencies
2. Enhanced rate performance
3. Relative stability

- Design effective strategies to **mitigate surface degradation** of integrated structures to improve and maintain their stability and rate capability when charged to high potentials (4.5-4.6 V).



Novel surface treatments for LLS



Unique surface modifications of layered-layered-spinel particles

Enable:

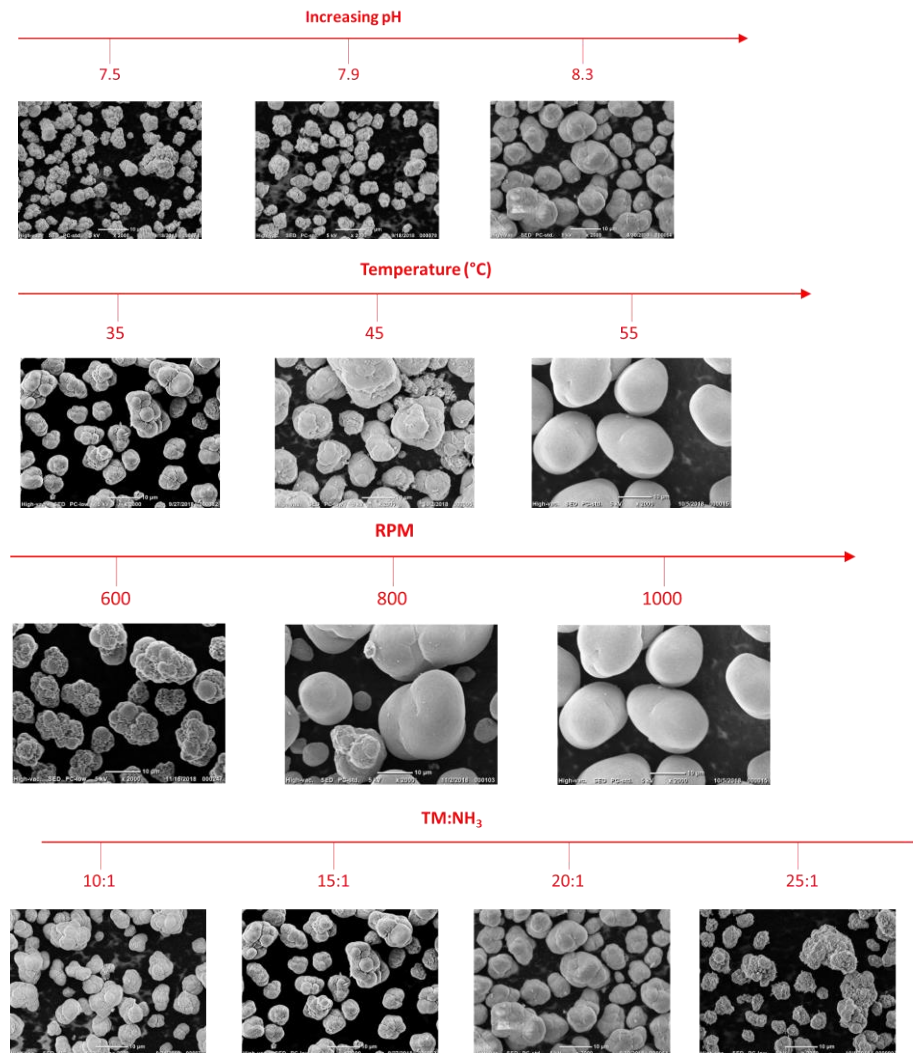
1. High capacity retention
2. Low impedance rise
3. Improved rate performance

4L CSTR Reactors



4L CSTR reactors used to study synthesis parameters of Mn-rich precursors including the effects of:

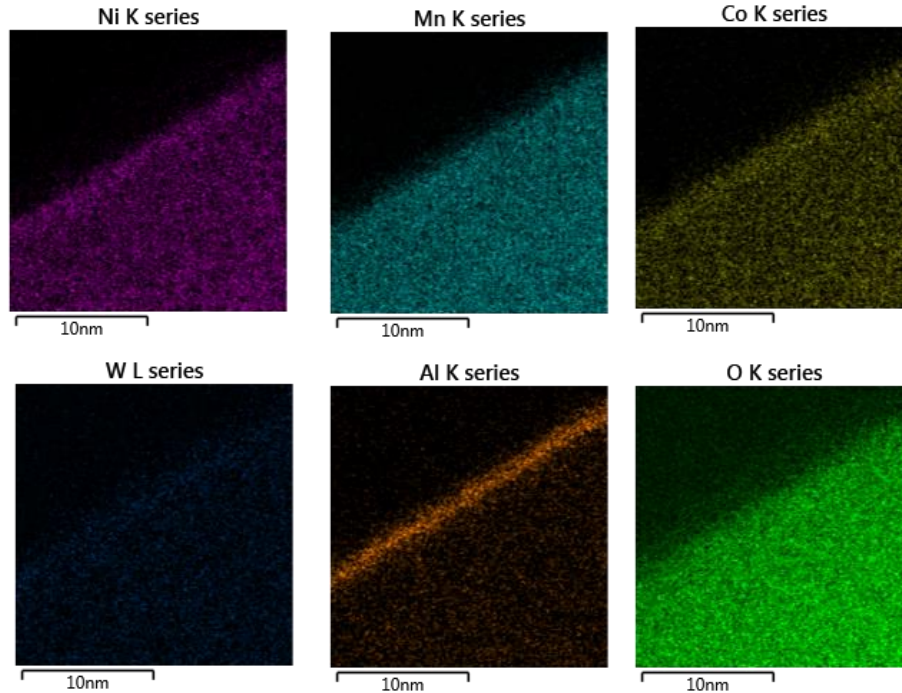
- pH
- Temperature
- Stirring speeds
- TM:NH₃
- Residence time



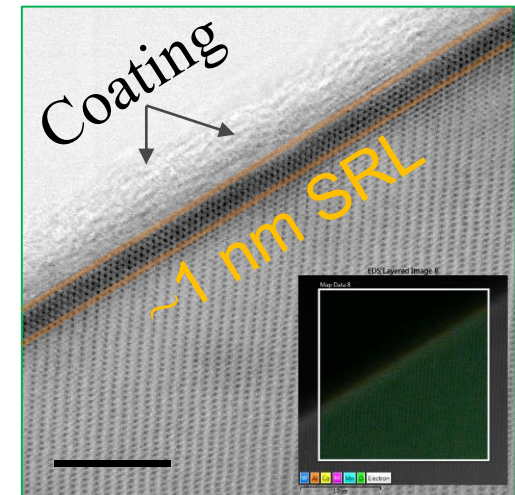
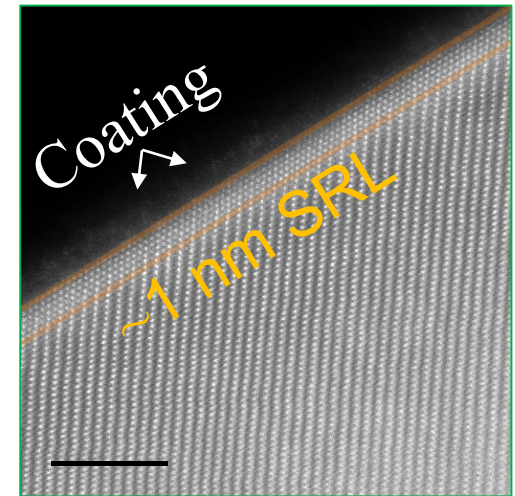
Synthesis parameters are being studied in order to precisely control particle size, morphology, density, and composition

Atomic Layer Deposition on LLS Cathodes

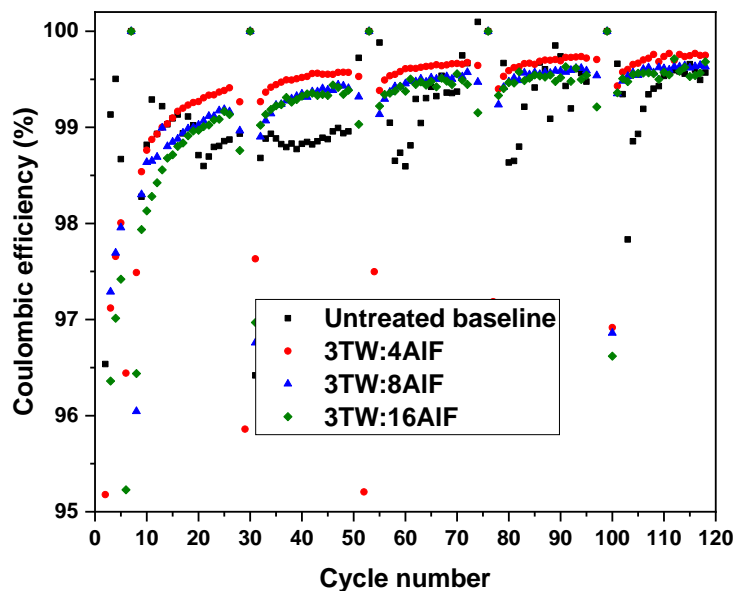
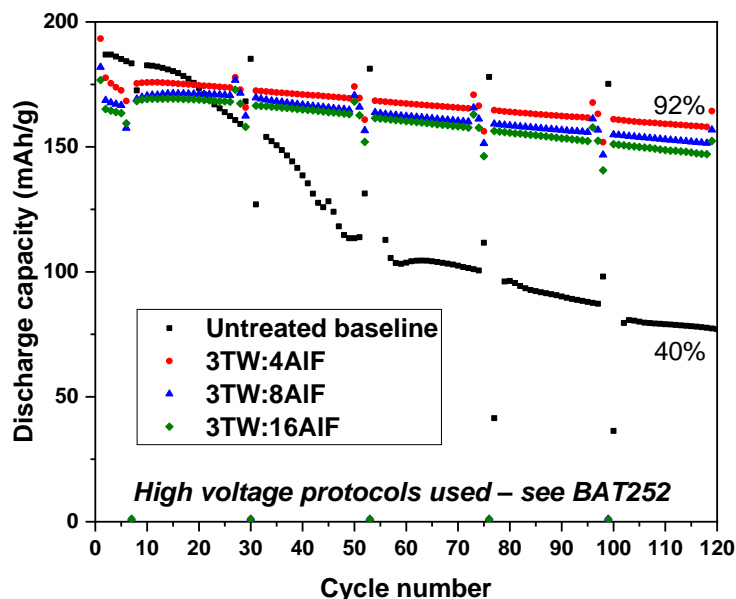
Technical Accomplishments



- A bilayer coating based on Al-W-F was successfully developed for deposition on layered-layered-spinel (LLS) cathode powders and electrodes using atomic layer deposition (ALD)
- W is uniformly distributed on the cathode particles
- A ~2-3 nm, Al-rich layer is detected on the surface – Al and F are the last elements deposited in the ALD coating process, resulting in a thin, low-average-atomic-number top layer



Novel materials are being developed for high voltage stabilization of Mn-rich cathode surfaces



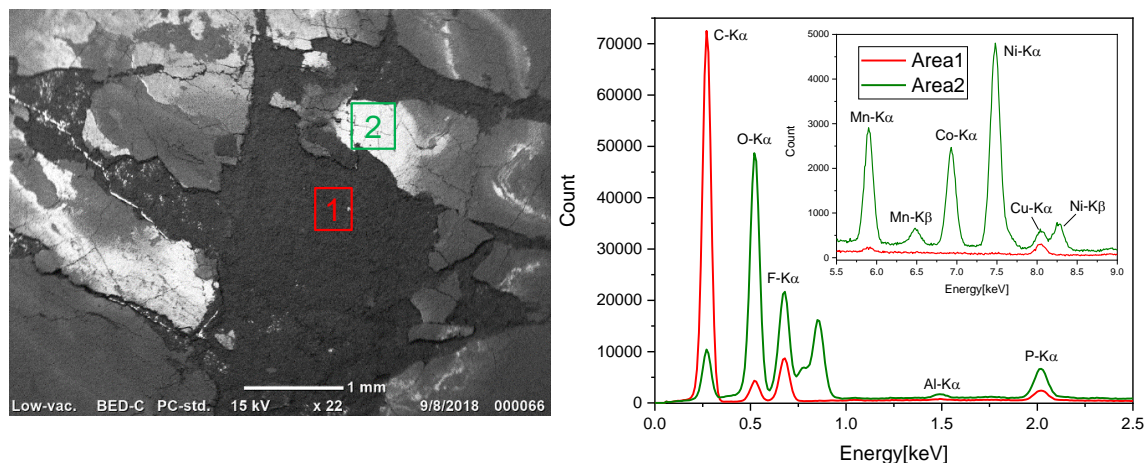
Composition	Thickness (nm)	
	TW	AlF3
3TW: 4AlF3	1.12	0.45
3TW: 8AlF3	1.05	1.1
3TW: 16AlF3	1.2	1.6

Thickness of coatings tested by modifying thickness of the Al-F top layer.

- Untreated, LLS baseline cathode loses 60% of initial capacity during full-cell testing
- Cycle life improved for all coating thicknesses – optimized performance (92% retention) was achieved with the thinnest top layer of Al-F (0.45 nm)
- First cycle coulombic efficiency (C.E.) decreased with coating thickness
- All coating thicknesses improved the C.E. of extended cycles when compared to the untreated baseline

New, bilayer ALD coatings show significant promise in stabilizing Mn-rich cathode surfaces

Analysis of anode cycled against uncoated cathode

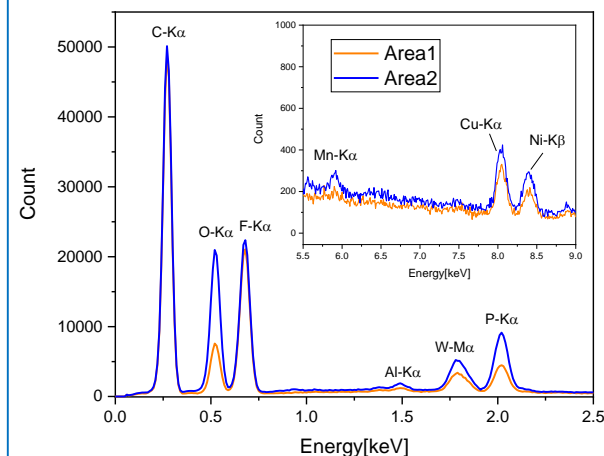
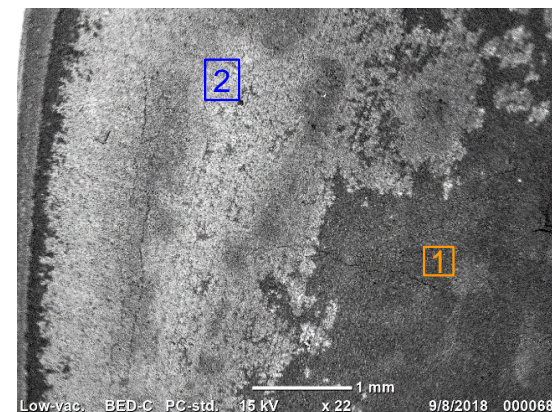


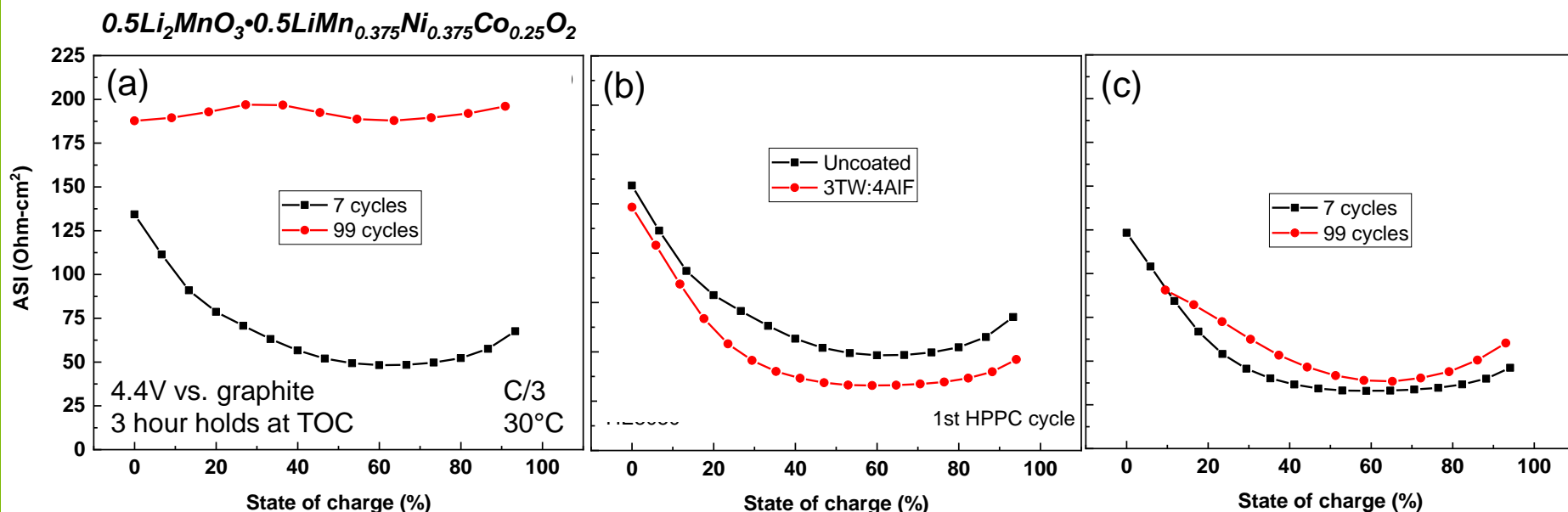
- Anodes exhibit two distinct regions after cell disassembly (labeled as 1 and 2 in SEM images) – more damage evident for the anode from the uncoated-cathode cell
- Energy dispersive x-ray spectroscopy (EDX) analysis revealed:
 - Significantly higher levels of Ni, Mn, and Co in the anode (region 2 – green) cycled against the uncoated cathode
 - Presence of W in the anode cycled against the coated cathode – no apparent effect on performance

Bilayer Al-W-F coating drastically reduces TM dissolution, significantly improving cycle life

*Color of EDX curves correspond to color of boxed region in SEM image

Analysis of anode cycled against 3TW:4AlF coated cathode

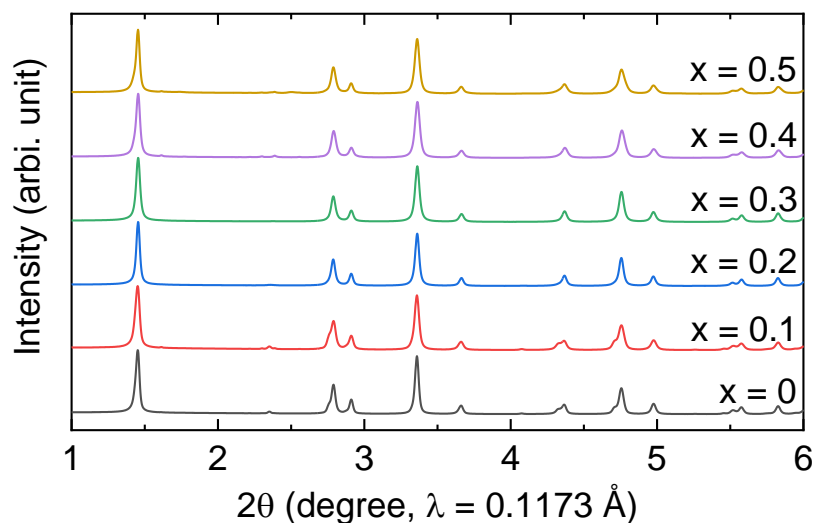




- (a) Uncoated Mn-rich electrodes show significant increases in area-specific-impedance (ASI) at all states of charge (SOCs) with high-voltage cycling (*100 cycles at 4.4V vs. graphite, 3 hour hold on each charge*) → Surface protection is necessary
- (b) Bilayer coatings result in lower initial ASI when compared to uncoated electrodes
- (c) Coated electrodes show striking improvement and reveal minimal growth in ASI with cycling at all SOCs, even under aggressive full-cell testing

Mitigation of surface degradation at high voltages due to newly developed ALD materials significantly improves impedance with cycling of Mn-rich cathode electrodes

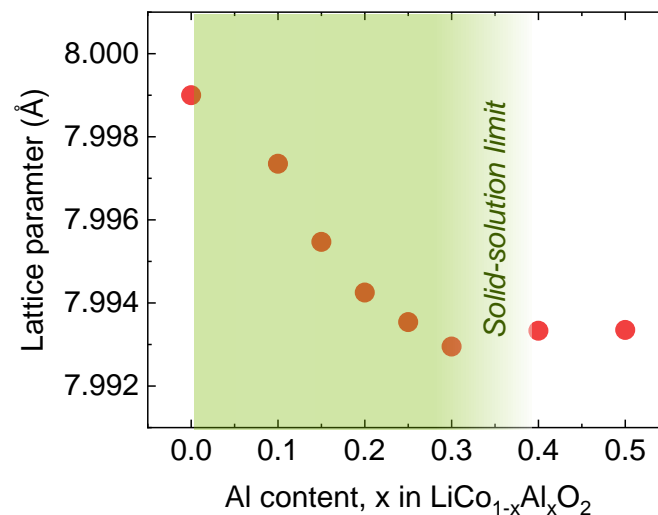
Novel Zero-Strain Spinel Cathodes: $\text{LT-LiCo}_{1-x}\text{Al}_x\text{O}_2$ Technical Accomplishments



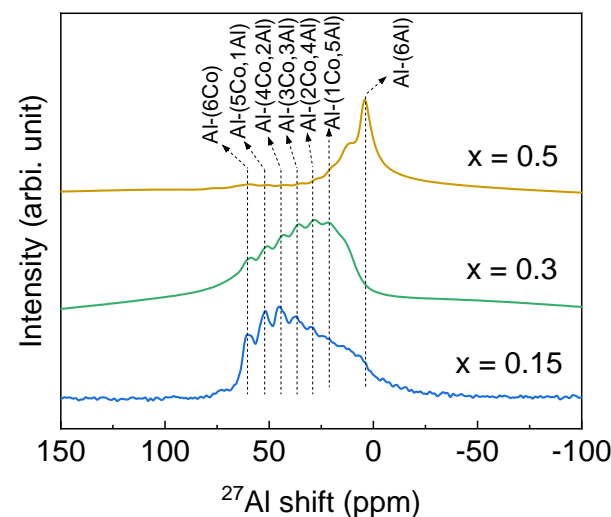
Synchrotron XRD of $\text{LT-LiCo}_{1-x}\text{Al}_x\text{O}_2$: The patterns for the cubic lithiated-spinel structure remain with partial substitution of Co by Al.

- Al substitution stabilizes the cubic lithiated-spinel structure
- Bulk lattice substitution of Al for Co is confirmed by the lattice parameter changes and ^{27}Al -MAS-NMR analysis
- The solid-solution limit is <40%

New materials for integrated, LLS cathodes have been developed with novel properties

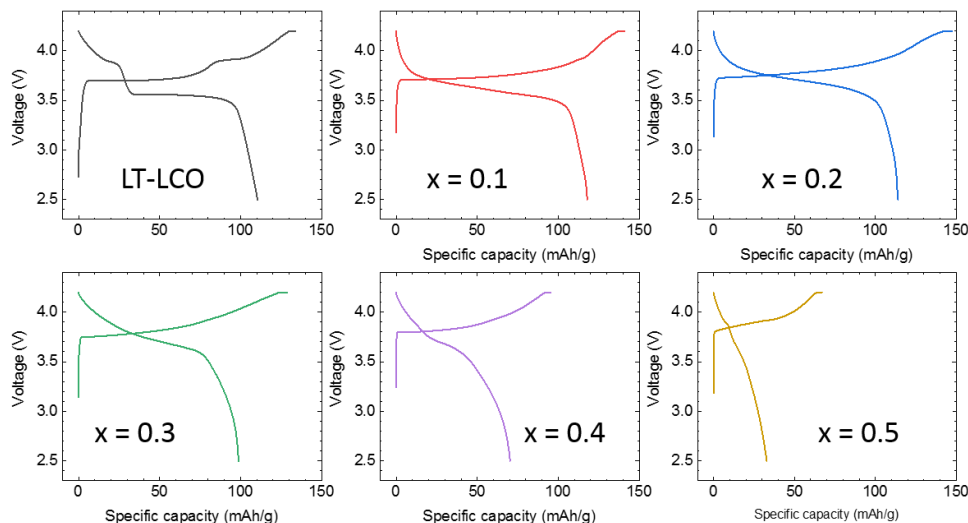


Lattice parameter decreases marginally with increasing Al content up to 30% substitution.



^{27}Al -MAS-NMR spectra: The $x=0.15$ and 0.3 samples show six distinct peaks at 23-60 ppm corresponding to Al in bulk lattice having varying numbers of Co nearest neighbors.

Novel Zero-Strain Spinel Cathodes: $\text{LT-LiCo}_{1-x}\text{Al}_x\text{O}_2$ Technical Accomplishments

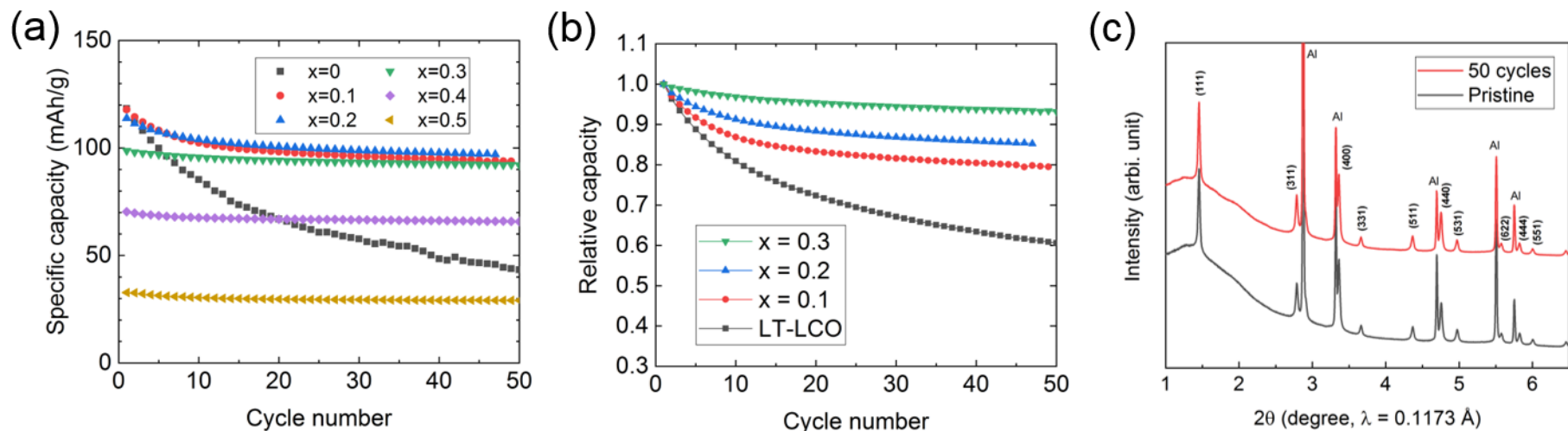


- Al substitution changes the Li intercalation mechanism from two-phase type (flat profile) to single-phase type (sloping profiles) behavior
- Partial Al substitution improves the specific capacity and the utilization of the $\text{Co}^{3+}/\text{Co}^{4+}$ redox
- The average voltage increases with increasing Al content

Initial voltage profiles of $\text{Li}/\text{LT-LiCo}_{1-x}\text{Al}_x\text{O}_2$ cells cycled between 2.5 and 4.3 V vs. Li at 15 mA/g.

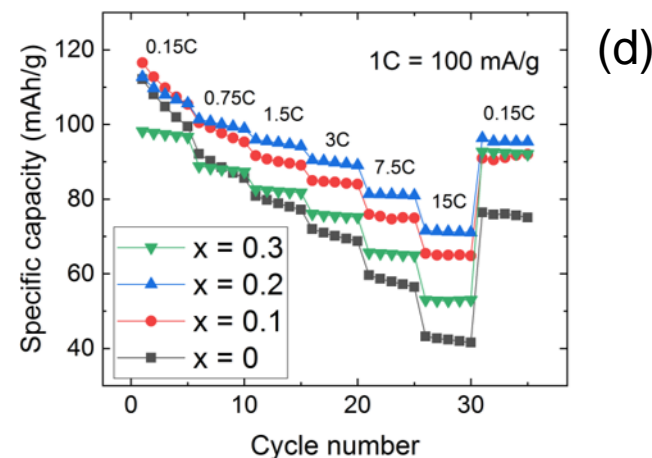
Theoretical and experimental properties of $\text{LT-LiCo}_{1-x}\text{Al}_x\text{O}_2$ electrodes

Sample: x in $\text{LT-LiCo}_{1-x}\text{Al}_x\text{O}_2$	Molecular weight [g/mol]	Theor. Cap. $\text{Co}^{3+/4+}$ redox [mAh/g]	1 st charge capacity [mAh/g]	Extracted Li [mol]	Co redox utilization [%]	1 st discharge capacity [mAh/g]	Coulombic Efficiency (%)	Average voltage [V vs. Li]
x = 0	97.873	273.8	133.8	0.49	49	110.4	83	3.60*
x = 0.1	94.678	254.8	141.0	0.50	55	117.9	84	3.68
x = 0.2	91.483	234.4	147.5	0.50	63	113.9	77	3.73
x = 0.3	88.288	212.5	128.8	0.42	61	98.8	77	3.76
x = 0.4	85.092	189.0	95.3	0.30	50	70.3	74	3.72
x = 0.5	81.897	163.6	66.9	0.20	41	32.8	49	3.72



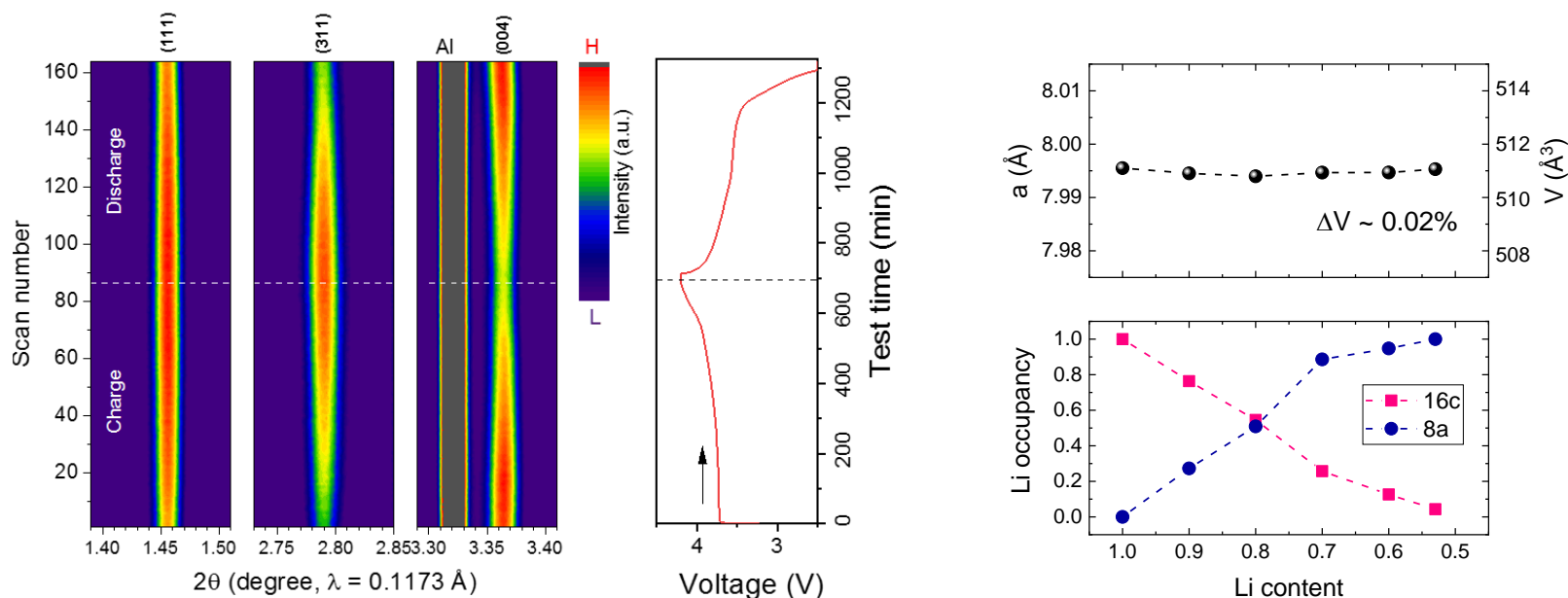
*Cycling stability of $\text{LT-LiCo}_{1-x}\text{Al}_x\text{O}_2$ electrodes: (a) specific capacity vs. cycle number plot, (b) relative capacity plots, and (c) *ex situ* XRD for $x = 0.3$ electrodes showing no degradation in structure after 50 cycles.*

- (a, b) Al substitution significantly improves cycling stability of lithiated-spinel $\text{LT-LiCo}_{1-x}\text{Al}_x\text{O}_2$ electrodes, optimum Al substitution range is $0.1 \leq x \leq 0.3$
- (c) The lithiated spinel structure remains unchanged after cycling
- (d) Rate performance is also improved by Al substitution



Comparison of rate performance: the $x = 0.2$ electrode shows the best rate performance.

Stability and rate are greatly improved through dopant composition



In situ synchrotron XRD of the $\text{LT-LiCo}_{0.85}\text{Al}_{0.15}\text{O}_2$ electrode: The pattern shows virtually no change in the lattice parameter. The reversible changes in the relative peak intensities correspond to the reversible migration of Li ions from the octahedral (16c) to tetrahedral (8a) sites during Li deintercalation.

- $\text{LT-LiCo}_{1-x}\text{Al}_x\text{O}_2$ has zero-strain behavior that is unprecedented in terms of its small volume change ($\Delta V \sim 0.02\%$, compared to 0.2% for $\text{Li}_4\text{Ti}_5\text{O}_{12}$) and high operating voltage ($\sim 3.7 \text{ V vs. Li}$) – *highest ever reported for a zero-strain Li electrode material*
- The occupied Li sites switch between the 16c octahedral and 8a tetrahedral sites as in $\text{Li}_{4+y}\text{Ti}_5\text{O}_{12}$, but the arrangement of the occupied 8a and 16c sites appears to be random

Mechanism of novel properties revealed in terms of structure and site-occupancy of dopant

- Practically relevant, Mn-rich particles are being developed through detailed studies of how co-precipitation reaction parameters control particle size, morphology, density, and composition
- New** materials for surface protection of Mn-rich cathodes have been developed leading to *significantly* improved:
 - Capacity retention (92% vs. 40%)
 - Coulombic efficiency during extended cycling
 - Impedance characteristics with high-voltage cycling
- Novel**, lithiated spinel, $\text{LT-LiCo}_{1-x}\text{Al}_x\text{O}_2$ materials, characterized by *near-perfect zero-strain behavior* ($\Delta V \sim 0.02\%$) and the *highest reported operating voltage* ($\sim 3.7\text{ V}$), have been developed as tailored components for integrated electrode structures
- The mechanism by which Al substitution modifies the Li intercalation energetics of spinel based materials (***improved cycle stability, increased operating voltage, transition to single-phase mechanism***) has been identified – *exciting implications are revealed for the design of new, high-performance cathodes for next generation Li-ion and all-solid-state batteries*

Comparison of lattice volume changes and average operating voltages of several electrode materials.

Electrode	$\Delta\text{Vol.}^{[1]}$	Avg. V
$\text{Li}_{1+y}\text{Mn}_2\text{O}_4$	5.6 %	3 V
$\text{Li}_{4+y}\text{Ti}_5\text{O}_{12}$	0.2 %	1.5 V
$\text{Li}_{1+y}\text{Rh}_2\text{O}_4$	0.5 %	3 V
LT-Li_{1-y}(Co,Al)O₂	0.02 %	3.7 V
HT-Li _{1-y} CoO ₂	3 %	3.9 V

Structurally integrated, Mn-rich cathodes continue to show improvement towards practical implementation under the strategies developed by this project

Response to Previous Year Reviewer Comments

General Comments

- The reviewer remarked that the potential merits of high capacity (high energy density) and low-cost have been demonstrated.
- The reviewer said that the stabilizing surface treatment with the approaches...has been successfully addressed.
- The reviewer expressed that this project has a generally good approach to the discovery and validation of LLS cathode materials. The reviewer stated that based on the history of the project team, the reviewer is confident in the quality of the work that underlies this project....

Response

- We thank the reviewers for the encouraging comments and constructive evaluations given on our work in developing Mn-rich cathodes.

Response to Previous Year Reviewer Comments

General Concerns

- ...the project's research summary slides are relatively vague (i.e., on the surface modification and the role of electrolytes on stability). The reviewer would have appreciated additional explanation into the materials synthesis methods and the selection of LLS compositions or modifications.

Response

- A more detailed understanding of the role of low-temperature surface treatments with respect to impedance rise and stability are currently underway including simulation efforts. The synthesis of the LLS materials follows a general (2 step) strategy used by industry which includes 1) the co-precipitation of a transition-metal (TM) precursor followed by 2) firing the TM precursor with lithium carbonate to achieve the final cathode oxide. The ratio between lithium and transition metals (Li/TM) is important in determining the amount of spinel in the final material. By lowering the Li/TM ratio in a step-wise manner one can achieve higher amounts of spinel. The optimum amount of spinel will exhibit the highest first cycle discharge capacity and coulombic efficiency before a quick decline in those parameters occurs as more spinel is introduced into the structure. In general, the optimum amount of spinel has been experimentally observed to be between 5-10%.

Response to Previous Year Reviewer Comments

General Concerns

- a state-of-the-art cathode material such as NMC-622 or NMC-811 should be used to demonstrate the benefit of these materials to energy density, rather than using NMC-532, despite NMC-532 being closer in stoichiometry to the LLS.

Response

- At the outset of this project NMC-532 was being produced on large scales by our industrial partners. At that time, NMC-532 was one of the industry standards and was chosen as a baseline for these studies for that reason. Recently, NMC-622 has become the commercial standard for NMCs and it is/will be used going forward for evaluation of our cathode materials. NMC-811 is not commercially available in electric vehicles because it does not cycle well and has troubling safety characteristics. NMC-811 is a material in development and is therefore not considered as a 'benchmark' cathode.

Response to Previous Year Reviewer Comments

General Concerns

- The reviewer suggested more detailed cost analysis to compare with NMC-532 and to provide more evidence that this is a low-cost cathode material. The reviewer also suggested that future work to add to the understanding of the capacity fading mechanism of the large pouch cell with this new cathode material, so that the continued improvements can be addressed.

Response

- Recent published work (J. Power Sources, 403 (2018), 56-65) on the cost analysis of various cathode materials estimated the price of Li- and Mn-rich NMC's to have the lowest cost (\$12/kg) for large volume production when compared to NCA (\$15/kg), NMC-111 (\$20/kg), NMC-622 (\$17/kg) and NMC-811 (\$14/kg). One of the major contributors to the capacity fading mechanism in full-cells containing Li- and Mn-rich cathode with graphite anode is Mn dissolution and crosstalk which leads to unwanted secondary reactions, as demonstrated in our FY17 presentation. The strategy to mitigate the effects of Mn dissolution has been to use surface modifications achieved by various methods (i.e. electrolyte additive, ALD coating, wet-chemistry surface treatments) shown herein and in the FY17 report.

Proposed Future Research

- This project is complete – Future work on Mn-rich electrodes for subsequent projects will focus on
 - Integrating novel spinel components (as described herein) for improved stability and cycling performance
 - Design of reactor synthesis parameters to achieve dense Mn-rich precursors
 - Improving impedance
 - Surface engineering
 - Studies on the thermal stability and gassing properties of LLS systems